The Rate of Interdiffusion of Sodium Hydroxide and Hydrochloric Acid By A Calorimetric Method

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY PURE SCIENCE IN COLUMBIA UNIVERSITY

BY
ALLEN KAY SMITH, B.S., M. A.

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ACKNOWLEDGMENT

The author wishes to express to Professor Frederick Barry his sincere thanks for the suggestion of this problem and his generous assistance, advise and inspiration throughout the course of this investigation.

He also wishes to thank the Department of Physics of Columbia University for the loan of certain apparatus that greatly facilitated the completition of the work.

DEDICATED TO MY WIFE
MARIE CALVERT SMITH

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INTRODUCTION

Physicochemical determinations which necessitate the measurement of electrode potentials are limited in their accuracy and scope because we have at present no means of estimating the values of the liquid contact potentials which are established wherever dissimilar solutions are placed in juxtaposition, as for instance in the salt bridges. In the absence of definite knowledge in this matter, many formulas have been deduced from purely theoretical premises for calculating these junction potentials. Among the most important are those presented by Nernst[1], Planck[2], Henderson[3], Lewis and Sargent[4] and Mac Innes[5].

Nernst's equation, which applies to the junction potentials of concentration cells, was derived from his theory of osmotic pressures and in its workable form includes the assumptions that the ions have equal activities and that the activity ratios are equal to the conlentration ratios; it is therefore, valid only as a limiting law. The equations of Planck and of Henderson, on the other hand are applicable to all kinds of liquid junction potentials; the two formulas however yield different results for most types of electrolytes because, while Planck assumed an initially sharp boundary line between the two solutions in contact, Henderson assumed, on the contrary, their immediate mixture. Planck also deduced an equation for the junction of electrolytes having four dissimilar univalent ions. Fales and Vosburg[6] have examined this formula in connection with contact potential differences between potassium chloride and hydrochloric acid and have found it to be invalid at 25° for liquid junctions of X M KCl-1.0 M HCl and X M KCl-0.1 M HCl where X ranges from 0.1 to 4.1. Lewis and Sargent modified this equation by substituting the molecular conductance ratios for the ratio of the sums of the mobilities of the ions; this modification however corrects only for change in mobility of the ions due to change in concentration. The MacInnes formula while based on fewer assumption than the others and possibly accurate to 0.3 millivolts, is applicable only to junctions of the same electrolyte.

From this brief discussion it is evident that the formulas thus far presented are either based on unverified and conflicting assumptions, the choice between which is largely pure guess work, or are applicable to particular combinations of electrolytes. They

(1) Nernst, Zeit. Phys. Chem. 2, 613, (1888); 4, 129 (1889).
(2) Planck, Weid. Ann. 39, 161, (1889); 40, 561, (1890).
(3) Henderson, Zeit. Phys. Chem. 59, 118 (1906).
(4) Lewis and Sargent, J. Am. Chem. Soc. 31, 363 (1909).
(5) MacInnes, J. Am. Chem. Soc. 37, 2391 (1915).
(6) Fales and Vosburgh, J. Am. Chem. Soc. 40, 1921 (1918).

are, consequently, of little or no value in precise experimental work, excepting perhaps in special cases; and the desirability of a few experimental data with which to test the assumptions upon which they severally rest is correspondingly clear.

Since liquid contact potential is a phenomenon always associated with the interdiffusion of the electrolytes employed in the salt bridges and is generally assumed to be caused by the interdiffusion of the ions of the two solutions, then if this assumption is true, it should be possible to calculate its value, without the aid of any doubtful assumptions, from the rate of interdiffusion, if this can be precisely determined. It is also of importance to know in this connection the extent of unavoidable initial mixing when the electrolytes are brought in contact with each other and the subsequent influence of this mixing on the interdiffusion rates.

An examination of the literature which bears upon these matters discloses the surprising fact that very few attempts have been made to determine experimentally the course of interdiffusion. Besides the early work of J. J. Thompson[7] and Graham[8], practically all we have are some incomplete experiments by Osborn and Jackson[9] in which it was attempted to measure, by an anlytical method, the diffusion of salts in the presence of other salts. Osborn and Jackson were unable to interpret their results but their work was later repeated and explained by Walpole[10]. From this meager exhibit of experimental results it appears that scarcely a beginning has been made toward a real solution of the physicochemical problems presented by the phenomena of interdiffusion. The work so far done in this field is practically barren of suggestion and as will be shown elsewhere, its results are of dubious value.

With these facts in mind the present work was undertaken in the hope of developing, first of all, a general method for the precise measurement of interdiffusion rates in liquid systems; since obviously the possession of such a method is the necessary prerequisite for further advance.

(7) J. J. Thompson mathmatical and physical papers. Vol. 3 pg. 428.
(9) Osborn and Jackson, Biochem. J. 8, 246 (1914).
(10) Walpole, Biochem. J. 9, 132, (1915).

METHOD OF PROCEDURE

It is evident from theoretical considerations, as will be shown below, that the direct observation of the interdiffusion of liquids by optical methods is quite impractical. Since also the method of chemical examination of samples withdrawn from the system is a rough procedure and quite inadmissable excepting for preliminary work, it was determined in this investigation to attempt the measurement of the rate of interdiffusion by estimating at short intervals of time the total heat developed as mixture proceeds. This heat, obviously, will be proportional to the quantities mixed, and hence its rate of evolution will measure the rate of interdiffusion.

The problem thus presented involves several experimental difficulties. First, it must be known in advance that with the system employed mixture is due exclusively (within error of observation) to diffusion and not to turbulence of any sort. Second, since the system cannot be stirred the determination presents a calorimetric problem of a wholly novel character; that is, the determination of heat developed in an inhomogeneous system, and this is not with reference to the initial and final conditions alone, but with reference to the actual rate of thermal change. No such measurement has heretofore been attempted, and is quite impossible excepting by a method which permits the exact measurement of small increments of heat during long periods of time under conditions which render the thermal leakage rates minimal and their variability in different parts of the system negligible.

The first of these experimental difficulties may be assumed to be overcome if in the first place optical observations under conditions similar to those to be employed show that the liquids to be used may be placed together with small initial turbulence, and that thereafter under circumstances no more favorable than those of the measurement they exhibit no observable irregularities of movement. The actual attainment of negligable turbulence thereafter may be assumed, if in calorimetric determinations the rate of heat development exhibits a regularity which is reproducible in successive repetitions of the same experiment.

It is clear enough that the second, that is the calorimetric problem, involves the greater difficulty. A procedure for the precise control and measurement of thermal leakage during long periods of time has recently been developed by Barry[11]: the adaptation of such procedure to the control of inhomogeneous systems, however, appears at first sight to be dubious. Quite obviously the general calorimetric control of inhomogeneous systems is impossible. It is conceivably practical, on the other hand, with systems in which the thermal gradients are so systematically distributed that they may be perfectly integrated by thermometers suitably placed; or in which, this having been accomplished with small error, the variation from symetrical distribution may be determined by subsequent measurements of local temperatures from which the total irregularities may be summated and corrected for. It is likewise clear that inhomogeneous systems will be measurable only when the thermal gradients within them are comparatively small. The

(11) Barry, J. Am. Chem. Soc. 42, 1295 (1920): 42, 1911 (1920) 44, 899 (1922).

difficulties to be anticipated when large gradients occur are not indeed the consequence of the inevitably larger errors in their determinations: a greater embarrassment results from their effect upon leakage. Ordinarily, in corrections for leakage, a partically isothermal calorimetric surface is assumed. This is not attainable with inhomogeneous systems unless the gradients near the surface are small enough to be effectively equilibrated by the vessel wall; or unless they are of such magnitude that they do not appreciably affect the practical uniformity of the leakage rate for different areas of the calorimeter and bath.

Fortunately in the case of diffusing liquids, the conditions are highly favorable in all of these respects: first, the systems are, with a variability which for reasons hereafter given may be anticipated to be slight, radially homogenous; that is the temperature of horizontal planes are sensibly uniform; second, the heat developed is small and its rate of evolution is slow. The radial homogeneity will be disturbed by the greater conductance of the walls of the containing vessel and of the thermometer as well as of other parts which may traverse the system vertically. Thus the high conductivity of the wall, which is desirable for the equilibration of leakage, operates unfavorably upon the radial homogeneity of the system. The magnitude of these effects could not be calculated in advance: provision had to be made therefore, for their separate estimation. (p. 21) Granted an effective continuous control of total thermal leakage therefore the slow evolution of heat may be considered advantageous for since it may be measured with a precision equal to any heretofore attained in the measurement of quickly completed processes, it permits the distribution on the calorimetric surface of small temperature gradients, the influence of which on the measurement may be corrected for. On the other hand, since it reduces the temperature range covered in any convenient time of experiment, the slow rate of change is unfavorable thermometrically. It was foreseen that in actual procedure it would be necessary so to choose a reaction, its initial temperature, and the concentration of the liquids used, that it would proceed at a rate (so far as may be anticipated) which would permit the measurement of a temperature range in a working day sufficient to secure as high precision as is compatible with the maintenance of small regional irregularities in the temperature of the calorimeter walls.

Such, in brief, were the general considerations which determined experimental procedure in the present research. These may now be specifically described.

THEORETICAL CONSIDERATIONS

A brief consideration of the mechanism of the interdiffusion phenomenon in electrolytes is desirable to make clear, before the actual experimentation is described, the general character of the chemical process examined; and at the same time more explicitly to justify the experimental method employed.

It is necessary first to note that the interdiffusion of strong electrolytes cannot be compared with the expansion of two gases into each other as might be the case for non-electrolytes; and while the interdiffusion of strong electrolytes must be considered as molecular rather than ionic, because ions cannot diffuse independently, yet in all such systems, a systematic ionic exchange may set up which will destroy any possible analogy with gaseous mixtures. The ultimate condition of the system is that of a homogeneous distribution of the possible molecular combination of the two solutions, as well as of the

original electrolytes. For interdiffusion of di-ionic compounds, composed of equivalent ions, the ultimate molecular distribution would correspond to that of gases, but the diffusion process would not thus correspond, because the unequal mobilities of ions would cause ionic exchange, with the result that the most mobile molecular species would attain homogeneity first. For example, if the original solutions were nitric acid and potassium chloride, then since hydrochloric acid is the most mobile molecular species derivable from this combination, this would be the first to reach homogeneous distribution. In case the original compounds were not composed of equivalent ions, then the ultimate condition of the system would not be a homogeneous distribution of the original compounds but of the possible molecular combinations. As an example we may consider the interdiffusion of hydrochloric acid and potassium sulphate; a homogeneous distribution of these two solutions would give in each unit cube of the system a ratio of 2, 2, 2, 1, for the hydrogen, chloride, potassium and sulphate ions respectively, but the homogeneous distribution of the possible molecular species, namely hydrochloric acid, hydrogen sulphate, potassium chloride and potassium sulphate would give a ration of 3, 3, 3, 2, respectively.

Let us, now, examine as typical, the combination of sodium hydroxide and hydrochloric acid, meanwhile keeping in mind that only slight changes of statement would be necessary if a combination of salts were being considered. As is shown in figure 1. the lower half of the system contains sodium hydroxide and the upper half hydrochloric acid and the broken line is the original boundary between the two solutions. We shall consider the simplest case, namely that in which the concentration and volumes are equal and consequently depths the same. Now if the rates of diffusion of the ions composing hydrochloric acid and sodium hydroxide were equal, we should expect the boundary between the two to remain stationary throughout the diffusion process. However, since this is not the case, the boundary will change its position and move toward the slower moving molecular species, in this case downward. If we consider for the moment. only the molecular diffusion of sodium hydroxide and hydrochloride acid, since the distance through which the hydrochloric acid has to move from some region of fixed concentra-

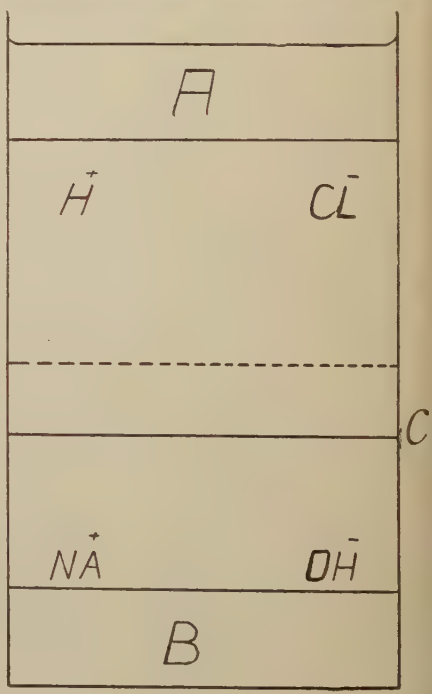

Figure 1.

tion A, (see figure 1), to the boundary plane is constantly increasing, and since the distance through which the sodium hydroxide has to move from its area of fixed concentration B to the boundary is decreasing, we should expect the boundary to adjust itself to some intermediate position, represented by the line C on the figure, which would be determined by the relative speeds of the ions. The actual position of the boundary plane however, cannot thus be precisely defined, because of the secondary diffusion of sodium chloride into the hydrochloric acid and sodium hydroxide and because of ionic exchanges. Further qualitative description of the phenomena is possible; but for the purpose of the discussion this much is amply sufficient to illustrate the complications of interdiffusion and to show that it is impossible to predict the ratios of the molecular species which occupy any given strata of the system at any given time. These complications limit the practical methods of measuring interdiffusion phenomena. The analytical method used by Osborne and Jackson, and Walpole, is not applicable for determining a continuous diffusion curve since one determination gives only one point on the curve and successive determinations would not be comparable because of the variation in the initial mixing. An optical study of the movement of colored ions in such systems would be interesting and instructive but it would be impossible to determine the process as a whole by this method. The refractive index method is eliminated because of ionic exchange. Thus it is evident that the attempted measurement of a rate of interdiffusion by any change other than that of energy, would include many uncertainties.

PRELIMINARY EXPERIMENTS.

Preliminay experiments were made with hydrochloric acid and sodium hydroxide as convenient solutions in order to observe the character of the boundary surface when they were placed in horizontal contact with minimumal disturbance. The interface was made visible by introducing into the acid or alkali a few drops of phenolphthalein or methyl orange. The experiments were made in glass tubes and vessels of several different diameters, that of the smallest being about four and that of the largest about fourteen centimeters. The hydrochloric acid was placed over the sodium hydroxide by two procedures illustrated in figures 2 and 3. In the first procedure, (Fig. 2) the diffusion tube was filled with sodium hydroxide solution to the top of a platform b and hydrochloric acid solution was then run in from a funnel to the platform which checked its downward fall so that it flowed out horizontally upon the alkali. In the 2nd procedure, illustrated in figure 3, the required amount of hydrochloric acid solution was placed in the diffusion tube and the sodium hydroxide solution then run out from its funnel to the bottom of the vessel. The final positions of the two solutions were the same in both cases. The platform b, in figure 3 was built to check the rebound of the alkali solution from the bottom of the vessel; it was unnecessary when sufficient care was observed in the initial part of the procedure. When equi-molar solutions of hydrochloric acid and sodium hydroxide are used the alkali has the greater specific gravity and must be placed in the lower position.

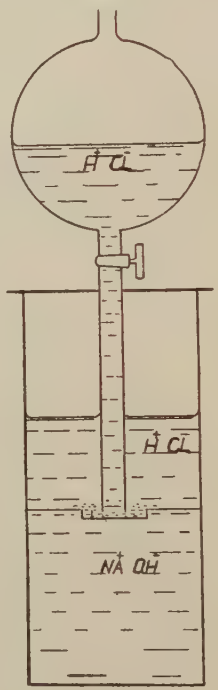

Figure 2.

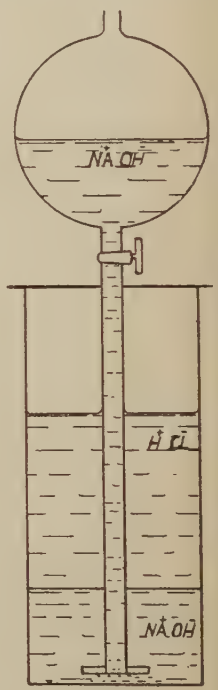

Figure 3.

By both procedures a very sharply defined boundary plane was obtained: its appearance might be described as that of a tender membrane between the two solutions. The system could be carried about the laboratory without causing much disturbance of the boundary; when the tube was gently rocked the boundary plane rocked with the solution and was only slightly broken; when the tube was brought to rest it gradually regained its original quiescence. On diffusion, the boundary plane moved steadily in the direction of the sodium hydroxide solution but it did not, observably, alter its character. In

order to define its limits of possible irregularity, the system was placed on a pier in a closet of constant temperature and observations made with a cathetometer telescope. In this way vertical distortion of a few hundredths of a millimeter could have been measured and smaller variations could have certainly been detected; but many observations over long periods of time showed that the surface of contact remained plane within this limit of variation.

These experiments supplied the welcome evidence that the solutions to be examined, and presumably any similiar solutions, could be superposed with very slight initial turbulence; that when thus placed they were not greatly disturbed by slight jarring of the system; and consequently after a short time succeeding their superposition it was highly probable that under conditions of experimentation, no mixing would occur excepting by diffusion. It may be remarked at this point that the very regular evolution of heat in the calorimetric determinations completely confirmed this anticipation. (P. 26)

It was likewise inferred from these tests that any horizontal zone of a system of this type would remain when undisturbed, thermally homogeneous, within narrow limits, the problem of measuring the temperature of such a system, consequently, resolved itself into that of finding the average vertical temperature. For this purpose a resistance thermometer might be used or a tube of staggered thermo-elements, or a mercury thermometer with a bulb equal in length to the depth of the liquid system. The resistance thermometer of the usual type introduces into the system a metal case which is undesirable because of its thermal conductivity; since a mercury bulb, unlike a staggered thermal is vertically homogeneous and has been shown to be sufficiently sensitive for use in the present calorimetric system, it was given preference in these experiments.

THE APPARATUS

The adiabatic calorimeter, as developed and described by Barry[11] was employed in these determinations, with the 40 mm. air gap between the calorimeter and water bath which Barry showed to be the most advantageous in this system. A new calorimeter was built which made possible some modifications and improvements on the previous designs.

It was especially desirable in these experiments, as will be shown later, that the heat exchange through any extruding parts of the calorimeter would be rendered inconsiderable and the correction for imperfect adiabaticity made as small as possible. With these ends in view the air chamber or outer enviroment was reduced in size to a space 60x90x120 cm. and was constructed by building a heavy oak table, with a back like that of a chair of the desired height. To this back and to the equally firm top of the table the sides, front and top of the air chamber, which were essentially windows, were firmly anchored with bolts and hooks, so that the whole enclosure could be easily removed when desired. The entire apparatus would fill only one corner of the constant temperature room formerly used and could be put there if it were desired to secure a still more effective control. Working with this inclosed apparatus, the operator reads his thermometers with a telescope mounted outside. Apertures in the chamber were provided so that the reaction could be initiated by hand, and sliding doors in the front and rear supplied easy means for adjustment of its thermal leakage. Electrical heating coils were placed at the bottom and back of the chamber and shielded with asbestos board. The air within it was distributed by two fans and their effectiveness was confirmed by placing compared thermometers in various parts of the chamber and reading them as nearly as possible simultaneously.

The temperature of the chamber was controlled by a seven inch bimetallic regulator connected to a Bever[12] type of heater control.

The air surrounding the calorimetric system was thus kept constant within ± 0.03 degrees for a period of more than ten hours. This constancy does not represent the limits of precision attainable with this type of air chamber but was sufficient for the present needs.

Since, with the heat capacities usually employed in these calorimeters, the temperature change in most reactions commonly exceeds 0.1 degree, a device was placed on the regulating screw head of the bimetallic regulator, so that by a simple accessory mechan-

(12) D. J. and J. J. Bever, Ind. Eng. Chem. 15, 359 (1923).

ism, the screw might be adjusted during the course of the reaction from without, and the temperature of the air kept at all times within a few hundredths of a degree of the calorimetric temperature. With this semiautomatic control the outer environmental temperature in these experiments never deviated from the calorimetric temperature more than ± 0.07 degree during the course of determination.

The calorimeter and inner apparatus for placing the solutions is illustrated in figure 4. The dimensions of the calorimeter* are the same as those previously used by Barry[11]. The closely fitting cup which occupies the upper third of the vessel and contains one of the solutions during the period of initial adjustment to constant temperature, is hereafter called cup A when it carries a short delivery tube which delivers hydrochloric acid upon the upper surface of the sodium hydroxide below it; and is called cup B when this short tube is replaced by one that nearly reaches to the bottom of the calorimeter and delivers the sodium hydroxide at the lower surface of the hydrochloric acid. The method of delivery in the determinations was essentially like that of the preliminary experiments illustrated in figures 2 and 3 (p.10).

A needle valve attached to a screw within the calorimeter and operated from above by means of thoroughly insulated vertical rod which carried a head large enough to make the amount of its rotation observable permitted the release of the solution from the cup at any desired rate of flow. This device worked quite effectively if the necessary precautions were taken always to exclude air bubbles from the delivery tube by filling it with solution before placing it in the calorimeter. If no air was in the tube, the cup was completely emptied; otherwise delivery was incomplete: in a few cases of incomplete delivery, the data of the determination were invariably discarded without examination The two methods of delivery yielded perfectly concordant results; but that by which the alkali was delivered beneath the acid, using cup B, invariably showed much less initial mixing; and in certain cases, (see experiment 27 fig. 6) such turbulence was not detectable, the form of the diffusion curve being consistent with the same empirical formulation in the initial as well as in the later periods.

It was possible to insulate this particular calorimetric system with unusual completeness. Its only extruding parts were the rod by which the valve was operated and the thermometer. These passed through telescoped chimneys in calorimeter and jacket which were built according to previous designs and thoroughly packed with cotton wool.

All of the inner calorimeter parts were either of solid gold (valve and valve screw) or of copper heavily plated with burnished gold. In the determinations, the results of which were accepted for record, there was no visible corrosion of any metal which had been brought into contact with the solution.

The thermometers used were solid stem instruments each constructed especially for the present system. On these instruments each degree was of about 70 mm. length and

* Diameter of calorimeter 108 mm.

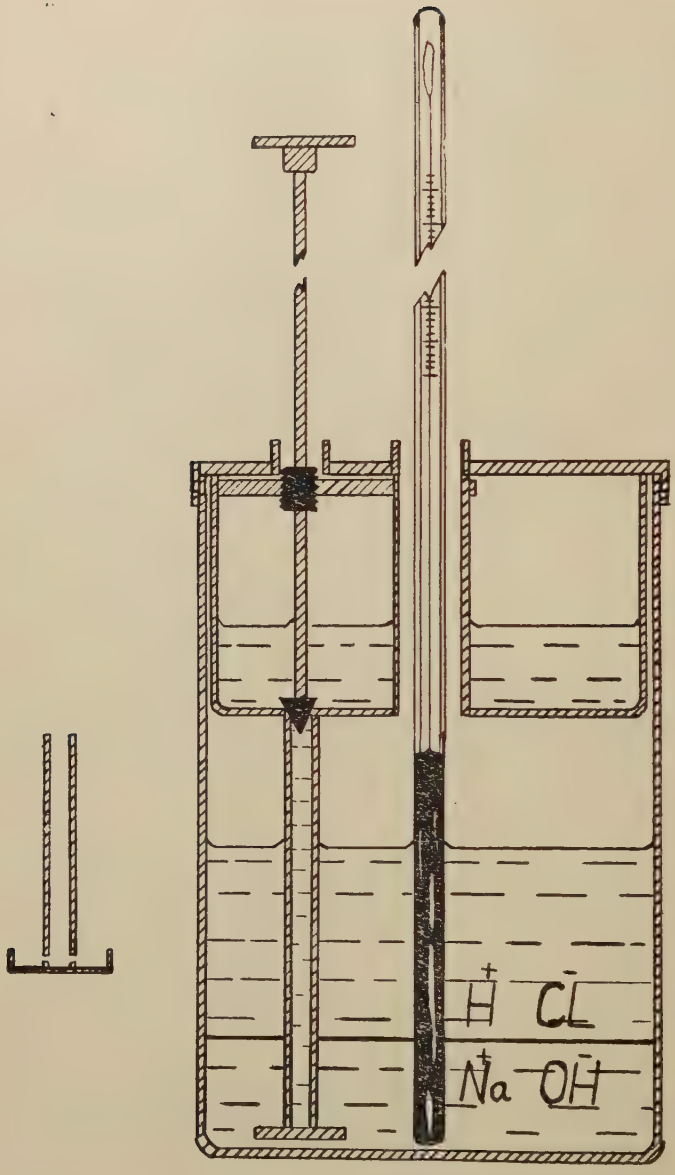

Fig. 4

was graduated to 0.01 degree, readings were taken by estimation with a telescope to 0.0005 degree, except during the preperiod, when slighter changes in temperature were detected by micrometer reading to 0.0002 degree. The bulbs of the thermometers had been made of a length equal within a millimeter to the depth of the liquid system; the glass tubing employed in the construction of the bulbs had been selected for its uniformity of diameter so that the bulbs were exactly cylindrical within less than .019 mm. The bottom and shoulder of the bulb had been made as nearly rectangular as was feasable with the thermometer construction. As a consequence of these precautions in the construction of these thermometers they almost exactly traversed the entire solution after mixture and thus determined the mean temperature of the liquid mass at its axis.

The bath was equipped with a mercury toluene thermostat regulator made of glass and coiled around the air jacket. This regulator like that of the air bath was connected to a Bever thermostat control so that the bath could be and was actually maintained at temperatures constant to ± 0.002 degree during each preperiod. The accessory thermostat was a very great convenience in experimentation since the temperature change in a still system well insulated, was always very slow. By use of the thermostat the initial isothermal condition in most of the final determinations is very conveniently attained by leaving the system in care of the thermostat overnight.

SOLUTIONS

The hydrochloric acid solutions used, were prepared by diluting Baker and Adamson's purest hydrochloric acid with an equal volume of water and distilling, using a quartz condenser. The second third of the distillate was used. This was diluted and standardized by the silver nitrate method, to the desired concentration within ± 0.0003 normal. The sodium hydroxide solutions used were freed from carbonate by precipitation with excess of barium hydroxide and the excess barium removed by addition of the exact amount of sodium sulphate solution. The alkali, having been standardized against the hydrochloric acid and adjusted to the desired normality, was preserved in paraffin lined bottles and properly protected from contamination with carbonate while stored.

THERMOMETRY

One mercury thermometer* was used throughout this investigation to determine the calorimetric temperatures; its twin instrument was used to determine the temperature of the bath; a single ordinary chemical termometer registered the temperature of the air chamber, after the uniformity of this temperature had been demonstrated. All these instruments were read from outside the air chamber; the calorimetric thermometer with a telescope, the other with a hand lens. Their comparative registrations were determined with care in the isothermal calorimetric system, those of the calorimeter and bath thermometers to $\pm$.001 degree. those of the calorimeter and air chamber thermometers to $\pm$.01 degrees and were recorded on immediately readable tables convenintly placed. On account of the small differences between the temperatures of calorimeter, bath and air chamber, the corrections for stemexposure were negligible, and since the immersions of the sensitive instruments were invariable in the determinations and the same within a few millimeters in the determinations and comparisons, no corrections for external pressure were necessary. Adequate care was exercised, also. to avoid error from parallax in all readings, and the illumination, though strong, was diffused, the reading error of the sensitive instruments was probably never greater than $\pm$.001 degree; the calorimetric instruments was probably never greater than .001 degree; the calorimetric instrument was habitually read by estimation to $\pm$.0005 degree. Neither of the two sensitive instruments though both were new, showed any change in the ice point during the entire series of measurements which could have affected any inferences drawn from the thermometric data.

The calorimetric thermometer was standardized directly to the thermodynamic scale by a method devised in 1922 by Barry and Webb, and since then developed in this laboratory into a facile, practical and exceptionally exact procedure. Since this method has not yet been described in any publication, and since its imployment in this research contributed materially to its practical improvement, it is here briefly explained, by permission; the occasion being favorable to the preliminary announcement. **

This method depends upon the possibility of maintaining for several hours in calorimetric systems a condition of practically complete adiabaticity[13]. Granted the control of thermal leakage in such a system within minute and precisely determinable ranges of fluctuation, it is evidently clear that thermal energy generated within it by the passage of an electric current through resistances suitably constructed and disposed may be measured with precision at whatever rate it may be developed. In previous standardiza-

* Described on page 19

**It is probable that within the year a full description of this method will be published, probably in the Journal of the American Chemical Society. The writer is indebted to Dr. Barry for such of the following memoranda as do not refer to the present research.

(13) Barry: The Maintenance of the Adiabatic Condition in Calorimatry. J. Am. Chem. Soc. 44, 899 (1922)

tions of thermometers[14] the procedure has been predetermined by the necessity of operating within sharply restricted time intervals in order to avoid indeterminate leakage of energy. The energy in these earlier attempts was supplied by a chemical reaction which has not only the disadvantage of the difficulty of converting such a standardization to absolute units but also the temperature coefficient of the reaction introduces a troublesome correction.

Under such unfavorable conditions the most skillful technique was unavoidably tedious, laborious and in the end none too dependable. It is probably for this reason that thermometers are still commonly standardized by indirect comparison with the normal hydrogen constant volume instrument, although the results of such comparison are, according to present standards of accuracy, very rough; being never wholly dependable within .002 degress. As a consequence, it is very generally believed that the mercury thermometer, in comparison with the electrical resistance thermometer and the thermoelement, is an inaccurate instrument: its use is unnecessarily restricted on this account, in favor of the employment of more elaborate installations; and its recognized practical advantages thus too commonly neglected. The highest accuracy in thermometry thus far attained by the use of the resistance thermometer and the thermoelement is in the neighborhood of 0.0002 degree: mercury thermometers standardized by the method here described register consistently and accurately to 0.0003 degree or less. In essential outline, the method of Barry and Webb is as follows:

Within a specially constructed calorimeter vessel similar to that used in the diffusion measurements here described, similarly insulated, and similarly controlled, the thermometer to be standardized is placed axially; and is surrounded by a cylindrical helix of doubled manganin wire, silk insulated, thickly shellacked and embedded in Wood's metal within a copper tube of about 5 mm. external diameter. The diameter of the helix is such that when the vessel is filled with still water and a current is passed through the coil, the heat developed is distributed as nearly as possible uniformly, so that in practice the necessary stirring of the system will be minimal. Provision is made for vertical reciprocating stirring by two-stage stirrers, one within the coil, the other outside it, which may be operated independently, or together in the same or in opposite phases. In practice the system is stirred at the rate of 12 strokes a minute: complete thermal homogeneity is thus quickly established, while the heat developed remains negligible during two hours or more[15]. The low melting metal which surrounds the wire ensures a very slight lag in the coil itself: the total lag of the system is only a few seconds, and since in practice it is constant, is negligible. The leads from the coil are so disposed that the very slight conduction of the wires will be practically constant under the adiabatic control. Other leads of very fine wire are attached to the ends of the coil, so that the constancy of its resistance during measurement may be occasionally tested. In this system the

(14) Richards and Thorvaldson: A new method for subdividing accurately a given interval on the thermometer scale. J. Am. Chem. Soc. 37, 81 (1915).

(15) Barry: Jour. Am. Chem. Soc. 44, 899 (1922).

heat capacity of which was about 1000 gram calorie units, the coil resistance was conveniently made about 13 ohms; its measured insulation resistance was 9 megohms.

In the present measurements the heating current was developed by a large accumulator, and reduced by proper resistance: after it had been run through the electrical system, shunted through an external resistance equal to that of the coil for several minutes, it was very constant. This current was run through a standard 10 ohm resistance and was controlled by high resistance rheostates in parallel to a constant potential difference across this resistance, as indicated by a Wolff potentiometer system of the usual type. The constancy of the potentiometer system was tested from time to time during measurement by substitution of a Weston Standard cell for the accumulator system. By these means it is easily possible to control the heating current to 1 part in 100,000 for any desired interval of time: in the present measurements it was constant to 1 part in 30 000. Since the standardization of 1 degree to ten thousandths necessitates a constancy of only one third this constancy, the standardization was therefore quite unaffected by variability in the power transmitted. Within similar limits of fluctuation also the coil resistance was constant during measurement; all the significant errors of the standardization were consequently calorimetric errors.

According to past experiences in this type of measurement a safe and convenient rate of energy supply was about five calories a minute, corresponding to a temperature rise in the system used of about .01 degree in two minutes. The rate employed in the present measurements was somewhat less than this, and readings were therefore quite unhurried.

By this method, times, not temperatures, are read. The slowly rising meniscus of the mercury thread in the thermometer is closely watched through a telescope, while the instrument is occasionally tapped by an attached electrical buzzer. Under these circumstances capillary friction (which with a good intrument seldom interferes with correct reading on a rising thread) is practically eliminated from consideration. As the meniscus approaches each 0.01 degree graduation mark, the tapping is made continuous; at the time of its occultation with the mark or at the instant it emerges from behind it, or at both times, a stop watch is set going, and is stopped at any convenient second thereafter as indicated by a well regulated watch. From these data the times at which the meniscus passes the 0.01 degree graduation marks may be determined with a precision of a few seconds, and under favorable conditions of illumination and magnification after a little practice, to within three seconds certainty: that is, when the rate of energy supply is adjusted to cause a .01 degree rise of temperature in from two to three minutes they are determined to within an error which corresponds to about .0001 degrees. It will be noted that these reading errors are not cumulative. At the end of the operation, the total time is taken with the same precision, that is with quite negligible error; and from these data by any convenient method of calculation (which is not excessively laborious if multiplication tables of 60's are used, and is simple when calculating machines are available) the thermometric corrections are readily derived.

It is obvious that the facility of the calculations is dependent upon the elimination of as many corrections for experimental errors as is possible. As already stated these should all be calorimetric errors. In the first determinations made by Barry and Webb

the leakage corrections were far from negligible, and their application tedious. The results were accurate enough, but their determination was protracted. In the present determinations the calorimetric corrections were so far reduced that for the short temperature intervals involved they were quite negligible. This improvement in the facility of the method was due entirely to the closer control of the outer environment, which made direct leakage by conduction and convection due to stirring negligible, and at the same time made very easy an exceedingly close adjustment of the bath.

This superior control had another result. In former standardizations, the operations required the simultaneous attention of two observers. In the present trials two observers also worked: but it was soon apparent that with a proper disposition of telescope and galvanometer scale, the whole apparatus could be managed by one observer without difficulty. The fluctuations of the heating current and of the environmental temperatures were so slow and minute, that it required only an occasional and momentary interruption of the readings to keep them in adjustment. The testing of the coil resistance and of the constancy of the potentiometer system necessitated the omission of one or two .01 degree readings, however, when the system was controlled by one operator.

By this method, it will be observed, the standardization consists of determined points at every .01 degree interval. This is an important advantage, since it practically eliminates all significant errors of interpolation. In the work of Barry and Webb these points were determined with an experimental accuracy, as shown by the extreme variations of four successive measurements of the scale degree interval, conduction under different rates of temperature change, of less than .0004 degrees; which indicated a probable error no greater than $\pm$.002 degree. In the present measurements a comparable accuracy was probably attained, the experimental controls being superior. It happened that the determined corrections for the small temperature intervals standardized were less than the estimated errors of reading.

IRREGULARITIES OF THERMAL DISTRIBUTION.

Since it was anticipated that the largest errors in these determinations would be caused by the thermal inhomogeneity of the system it was necessary to investigate experimentally its most significant effects.

First of all: the mean temperature of the system was to be taken by a mercury thermometer, the cylindrical bulb of which traversed the contained liquid vertically at the center. This procedure was based on the plausible supposition that the system was thermally homogeneous in the horizontal planes: to the extent that these isothermal surfaces were bent out of this precise position, the temperature measurement would be affected with error. It was necessary to determine whether or not this error would be significant, and if it were found to be significant, to correct for it.

Second: the correction for imperfect adiabaticity was to be based upon the supposition that the mean temperature of the calorimeter surface was that indicated by the central thermometer, although it was known that within the liquid the central levels would be warmer than those above and below, and that upper levels would be warmer than those at equal distances from the central zone, below, on account of convection. It had been presumed that the wall of the vessel would equilibriate the vertical heads considerably; but it was necessary, before the correction for imperfect adiabaticity could be accepted as dependable, to know two things: first, that the mean temperature of the wall was close enough to that indicated by the thermometer to make the necessarily large error in the correction applied to the leakage rate (and thus to the correction for imperfect adiabaticity) negligible; second, to know that the difference between the temperature of different areas of the wall was insufficient to produce convection currents in the air gap which would necessarily affect the predetermined rate of leakage for the conditions of experimentation which had been calculated upon the assumption of an isothermal surface.

There was only one way of determining these effects; namely that of measuring the local temperatures within the system; and for such measurements thermoelements were necessary. For their accomodation a special cover for the calorimeter was made, which carried narrow vulcanite boxes placed at right angles radially, within which thermals could be held, and by appropriate mechanism moved, either radially or vertically, while the system still remained effectively insulated. The arrangement was such that two thermals could be placed in the radius which was traversed by the thermometer and delivery tube, and one moved so as to span any portion of this diameter on the opposite side of the thermometer, while a forth could be similarly moved in a radius perpendicular to these; all in one assemblage of apparatus. Finally this radial movement could be effected at different levels: by one set of instruments between a level below the central zone and the surface of the liquid, and by another between a level above the central zone and the bottom of the liquid. Thus at the central zone and any set of levels above it or below it, the thermal gradients within the liquid could be determined on three radii from the central thermometer and the wall; so that, in case it should be necessary, the complete thermal distribution within the system could be roughly integrated and corresponding corrections for the measured temperatures deter-

mined at various stages of the diffusion. The rack and pinion mechanism which operated the radial movement was operated by a vertical vulcanite rod which carried a head and pointer above, the rotation of which measured the distances traversed by the moving arms of the thermels; the vertical displacement could be measured by the rods attached directly to the cases of the thermels, which were likewise brought out of the system.

The thermels were copper-constantan elements, with six junctions in each arm, encased in thin glass tubes and embedded in paraffin; each one therefore established a potential of about 250 microvolts for each degree of temperature difference between the two sets of junctions; with the galvanometer system used (which showed clearly fluctuations of 0.2 microvolt) it was thus possible to detect a temperature gradient of 0.001 degree, this sensitivity being considered sufficient for the present purpose. On acount of the construction of the calorimeter these thermels were subjected to no sudden or irregularly disposed temperature gradients; they were nevertheless, made of very good wire, which by the exceptional courtesy of W. P. White, had been tested in the Geophysical Laboratory at Washington for inhomogeneity and thus shown to be quite dependable, when properly arranged in the instruments over its whole length.

The writer wishes to express in this place his appreciation not only of this kind ness, but also of many helpful suggestions received from Dr. White which greatly aided the progress of the work.

In detail, the thermels were constructed in accordance with the techniques described by White[16]; they were satisfactory in every way.

In the thermoelectric measurements themselves it was unnecessary to use a complete potentiometer installation, since it was desired only to measure temperature differences known to be small. This was easily accomplished by using the galvanometer as a direct reading instrument as had been shown by White[17] to be practical for the determination of small potentials.

The thermels were calibrated by noting their effect upon the properly shunted galvanometer when they spanned a temperature difference of about two degrees, measured precisely to ± 0.001 degree (that is to 0.05%) by the mercurial thermometers. The change in the galvanometer deflection due to the parallel resistance necessarily included having been corrected for, the following results were obtained:

Thermal number	Deg/mm. deflection
1	0.004
2	0.006
3	0.006
4	0.0026

The sensitivity thus indicated being sufficient for the present purpose, the thermoelectric testing of the system was then undertaken. The galvanometer system offers a

(16) White, Jour. Am. Chem. Soc. 36, 1914.
(17) White, Phy. Rev. 25,334, 1901; Jour. Am. Chem. Soc. 36, 1868 (1914).

single peculiarity, which is worth nothing, that namely of the relatively high resistance of the thermoelectric junctions, which give to the formula by which the potential is calculated an unfamiliar cast.

The deflection for a given electromotive force is changed, by the presence of the shunt, in the ratio

$$\frac{(P+G)\,S}{(P+G)S+PG} = \frac{1}{1+\dfrac{PG}{(P-G)\,S.}}$$

Where P, S and G are resistances of the thermal, shunt and galvanometer respectively.

In these measurements, as well as those of calibration, the usual precautions were taken against stray thermo-electric forces, which were determined in each reading by the utilization of the eliminating switch. No shielding was necessary. The negligibility of external resistances, not accounted for by the formula, and in general the adequacy of the formula itself, was tested by the substitution of different shunt resistances in certain measurements otherwise identical: these measurements gave the same results.

A complete series of such measurements of the thermal inhomogeneity was not made because it was fortunately shown to be necessary, the various thermal gradients discovered being smaller than was anticipated. The following data are sufficient to indicate their magnitude. The measurements from which these were derived were made over a period of about an hour.

Vertical Temperature Gradients

Thermal No.	Elapsed Time In Minutes	Mm. Deflection	Temp. Diff. (degrees c.)	
	5			
4	17	5	.013	
4	19	3.2	.0087	Gradients close to wall in lower half of liquid
4	22	2.2	.0057	
4	25	2.0	.0052	
4	30	1.6	.0042	
4	55	1.0	.0026	
2	40	.3	.0018	Gradients close to wall in upper half of liquid.
2	65	.2	.0012	
1	66	.2	.0008	

Radial Temperature Gradients

The data for radial temperature gradients are not recorded here, since they were no greater than the slight deflections caused by the parasitic electromotive forces detected in the circuit at the times when they were measured. This negative result shows conclusively that in the diffusing liquids the horizontal planes are thermally homogeneous within 0.001 degree, and fully justifies the assumption that the long bulbed thermometer measures the mean temperature of the system. This result was somewhat surprising; but it had not been wholly unanticipated.

The effect of the thermometer and delivery tube, which penetrated the system vertically was known beforehand to be very small. The thermal conductivity of glass (0.015) and of mercury (0.019) are very nearly the same as that of water, while their specific heats are much less; it was thus conceivable that the thermel conductivity of the solution was greater than that of the thermometer. Similarly, although the copper delivery tube had a thermal conductivity approximately 650 times that of water, its heat capacity was only 0.7 gram caloric units, so that altogether the effect of its conduction was likely to be lost in the much greater heat capacity of the solution. It was clear furthermore, that the slight convection currents in the solution, such as are known to occur in the upper levels, would still further reduce the effect of all such conductances.

It might have been anticipated, also that the walls of the calorimeter would cause a superimposed temperature effect on the thermometer, that is, that the walls might conduct heat from the reaction zone to the upper and lower surfaces of the solution and then radially across the solution to the center. The dimensions of the system however were favorable to the prevention of this possibility, since the radius of the solution, 52 mm. was greater than the distance from the reaction zone to the surface, 49mm.

As a result of these thermoelectric measurements, the vertical gradients alone, therefore, had to be further examined those in the mass of the solution could be ignored, since the radial homogeneity assured their effective integration by the thermometer, however they varied. Those in the calorimeter wall, however, were serious, for reasons already given. By the process adopted these were not taken directly, as they might have been were the thermals embedded in the walls of the calorimeter. This procedure while feasible is exacting and laborous and not to be undertaken excepting of necessity. The gradients here measured, which were those of the solution close to the wall, were it will be noted greater, perhaps considerably greater, than those in the wall itself, and it is not impossible that they were wholly equilibrated by the wall. They were therefore extreme maximal gradients in this region * and any inferences derived from them with respect to error in the calculation of thermal leakage would yield excessive estimates. Now the maximum vertical gradient is of course in the lower layers of the liquid where convection is least. Let us assume then for the purpose of calculating a maximum error of heat exchange with the bath due to this inhomogeneity, that this gradient exists on the wall of the calorimeter. For this calculation let us divide the area of the calori-

* The absence of a radial thermal gradient within this system does not necessitate a vertical gradient in the wall identical with that of the adjacent solution; since the evolution of heat is continuous.

meter wall into two parts: first, that of which the mean temperature is above the mean temperature of the system and, second, that of which the mean temperature is equally below the mean temperature. These areas may be calculated with a fair degree of accuracy from the dimentions of the liquid system and the calorimeter, assuming for the purpose of rough estimation that the vertical gradients over the liquid depths are equal and linear on both sides of the central zone, and that the rest of the calorimetric surface is that of the surface and the bottom of the liquid. They are, first, 166 cm^2, and, second, 543 cm^2. If these areas were equal, their temperature differences would compensate each other so far as conduction leakage between the calorimeter and bath is concerned, since one is positive and the other negative to the same degree: the area to be corrected for [illegible] difference, which is 377 cm^2, or 53% of the total area. The predetermined leakage modulus for the 40 mm. air gap is 0.000011 degree per miuute per .01 degree bath head[18]. This modulus had been determined with reference to the entire calorimeter surface: in this case therefore the modulus will be 53% of 0.000011 or 0.0000053 degree per minute per 0.01 degree bath head. Now the mean total vertical gradient of the solution (and by assumption of the wall). for the first fifteen minutes of diffusion is by extrapolation from table (p. 23) is 0.04 degree; and considering that the thermometer is a the mean temperature of the liquid system, its extreme diviation from the mean is 0.02 degree. The total maximum error in the correction for leakage for the first fifteen minutes, then will be 0.0000053 x 2 x 15 equals 0.0002 degree. Similarly, for the next fifteen minutes the error will be 0.0001, for the next hour 0.0001 degree, and thereafter it may be assumed to be less than 0.0001 degree per hour. The maximal total error from this source for a complete determination lasting for 4.5 hours (the maximal time) cannot therefore be greater than the sum of these quantities, that is about 0.0006 degree. This error is but a little greater, or no greater than the thermometric error, and distributed over the whole measurement cannot affect the form of the curve of heat development. It may consequently be disregarded.

The final results of these thermo-electric tests, it is clear, completely justify the experimental procedure in the present investigation. It remains to describe the actual determinations of the diffusion rates.

(18) Barry. J. Am. Chem. Soc. 44, 899 (1922).

DETERMINATIONS OF DIFFUSION RATES

The first series of determinations of the diffusion rates, seventeen in number, were performed to develop the technic of the work and to examine the effectiveness of the various mechanisms, insulations and controls. None of the results of these experiments is included in the final results. Even after beginning the final series of determinations several measurements were rejected, prior to the calculation of results, because of known errors in technic.*

In each experiment of the second series, the results of which were, for the most part quite unaffected by accidental error, and therefore dependable, the concentrations of the hydrochloric acid and sodium hydroxide used were equal; and altogether determinations were made with three pairs of concentrations, namely 0.125, 0.250 and 0.500 normal. Measurements were made with all three concentrations in cup B and with concentrations of 0.125 and 0.250 normal in cup A.

In all of the experiments the solutions were approximately weighed out into the cup and calorimeter respectively; they were then adjusted to the nearest 0.1 degree of the desired temperature weighed again to the nearest 0.01 gram and quickly enclosed within the calorimetric system.

Since in the assemblage used, only the thermometer and the valve release rod projected from the calorimeter into the outer environment, since the parts through which these extruded were constructed and packed with cotton as in the procedure described by Barry[19], and since finally the system was unstirred, the transfer of heat between the calorimeter and the outer environment was at a minimum. During the preliminary period the bath was placed under control of the thermostat. During the period of the reaction it was kept closely adiabatic by adjustment of the bath to a fluctuating temperature which was always (excepting rarely by accident) within ± 0.008 degree of that of the calorimeter. This control was in these measurements for the first time supplemented by a close regulation of the surrounding air. In former work the temperature of the outer environment varied 0.1 and even 0.2 degree; in these determinations it was always within 0.07 degree of the calorimetric temperature and usually much closer. It is interesting to note that this better control of the air temperature not only reduced direct leakage into the outer environment, but also made the bath control far easier and much more precise. As a result of this more effective control of leakage, and because a record was maintained during the course of the experiment, with reference to which the positive and negative bath heads were always made nearly equal to zero at the close of the measurement the correction for imperfect adiabaticity was consistently negligible, although experiments lasted four hours or more.

In the construction of the apparatus no allowance had been made for measuring the

(19) Barry Jour. Am. Chem. Soc. 44, 889 (1922).

*They were not on this account without value. A subsequent examination of the data they provided showed that if all of them had been included in the final summary, the mean values accepted would have been no more than 5% in error.

temperature of the solution in the cup; it was therefore impossible to know when the two solutions had attained the same initial temperature. Although there was no reason to believe that an initial temperature difference of 0.001 to 0.002 degree between the two solutions would cause any error in the measurement of the temperature of the system after the reaction had been initiated, since the thermometer recorded the average temperature of the two solutions yet to secure an initial isothermal condition the preperiod was seldom less than three hours long, and in nearly all the final determinations the apparatus was set up on the preceding afternoon or evening and the system was given overnight to come to uniform temperature. In any case the reaction was not initiated until the temperature change did not exceed 0.001 degree, and was usually less than 0.0005 degree, in thirty minutes.

In figures 5 and 6 are plotted a series of results for the concentrations 0.125, 0.250 and 0.500 molar obtained by the two methods of delivery previously described. The points given are the experimental points, corrected only for thermometric irregularities. It should be particularly noticed that these curves are not in the least smoothed out; but are directly drawn through the determined points. The experimental curves with cup A (in which acid was delivered upon the surface of the alkali), may be identified by sharp maxima in the initial segments. These maxima are the results of the procedure used in superposing the solutions and are not shown by the curves of determinations made with cup B (in which the alkali was run in beneath the acid), nor when a short bulbed thermometer was used in preliminary trials. Some such irregularity might have been anticipated, because when the acid first comes in contact with the alkali the mixing of the two solutions causes a rapid rise in the thermometer reading, inasmuch as the thermometer bulb is only slightly more than half immersed and is in the warmer part of the divided system. As the acid continues to flow to its position above the alkali the thermometer bulb becomes completely immersed, and the reading drops to that of the average temperature of the system. The completion of the process of placing the solution is roughly indicated by the second rise in the curve. When cup B is used, this second rise, like the maximum disappears, probably because the initial mixing is considerably less, when the alkali is run in beneath the acid.

To locate the exact time when the effects of mechanical mixing caused by superposing the solutions stop, and the effects of diffusion alone begin is difficult. The technic of placing the solutions so far developed permits no prediction of the time of delivery nearer than two minutes. The character of the valve employed is partly responsible for this uncertainty. When the valve is seated firmly, to make sure that no leakage will occur, the bottom of the cup, which holds the valve seat, is sprung slightly, and the fraction of a turn of the valve head which is necessary to loosen it, is never the same. In the preliminary experiments with glass vessels, the shortest possible time for delivery was four minutes; under experimental conditions the time was always greater. From an inspection of the curves with cup A it will be seen that the second rise of temperature, with the exception of number 19, begins from five to eight minutes after initiating the reaction, so that it would seem safe to say that the delivery in every case except 19 was completed within ten minutes.

All of these diffusion curves are of the same form, within the range of variability

ascribable to experimental errors previously estimated. Since the conditions of the separate experiments those namely, of concentration, temperature range and degree of initial mixing, are widely different, a brief discussion is necessary to show that this is the case and that the phenomenon of interdiffusion therefore follows a definable law. This regularity of behavior may be exhibited in two ways: by superposing the curves, and by deriving from them an empirical mathematical formulation which will correctly define their common form in the segments which represent the undisturbed process of diffusion. The curves in Figure 5, of which 27 and 24 show the behavior of 0.125 molar solutions and the remainder, apply to 0.250 molar solutions, show clearly the results of accidentally varying the initial mixing. It could hardly have been expected that the curves as originally plotted would be parallel. The mixing of the two solutions changes their concentration near the boundary plane, and establishes a concentration gradient much more quickly than by the slow process of diffusion. Since, then, both the rate and the degree of mixing are variable the curves must have variable initial slopes under conditions otherwise similar. Whether the concentration gradient is established by mixing or by diffusion, however, the subsequent state of the system will be closely the same in all cases: the several processes measured, therefore, must have corresponding states, though these do not exist at corresponding periods of time after diffusion begins. In comparing experiments then, which show varying degrees of mixing, the curves of those in which greater mixing occurs must be transposed, and to the right, since time is plotted in this direction.

The extent of transposition is evidently some function of the degree of initial mixing. This relation is not generally determinable, since the rates and degrees of mixing cannot be independently measured. The curves may nevertheless be tested for parallelism by simple procedures. The simplest of these is applicable to curves which correspond to diffusions in solutions of the same concentration. It is carried out by first locating segments of equal slope on the two curves and then transposing the entire curves sufficiently to bring these segments into the same time interval. Here, evidently equal slopes mean equal rates of temperature change and thus equal rates of diffusion—that is to say, they represent comparable conditions. If then such slopes are brought into the same time interval and if the law of change is the same in the two cases compared, the curves will be parallel throughout their lengths in the period which succeeds to that of initial disturbance. For example on curve No. 20 fig. 5, the temperature rise from twenty to 80 miinutes after diffusion begins is 0.069 degree, while on curve No. 25 a corresponding rise is found between seventy and one hundred and thirty minutes after diffusion begins. Then considering the whole of the two curves after the period of initial disturbances is over, namely from twenty to two hundred and ten minutes on curve No. 20 and seventy to two hundred and sixty on curve No. 25 the corresponding temperature increments are 0.179 and 0.183 degree. This comparison shows a discrepancy between the two curves of 0.004 degree which is greater than the average for this method of comparison. A graphical representation of this procedure is found in figure 5 where broken lines indicate the transposition for several of the curves.

In order to compare determinations made with solutions of different concentrations it is necessary first, to multiply their temperature increments in comparable times by the factor necessary to compensate for their different rates of evolution of heat.

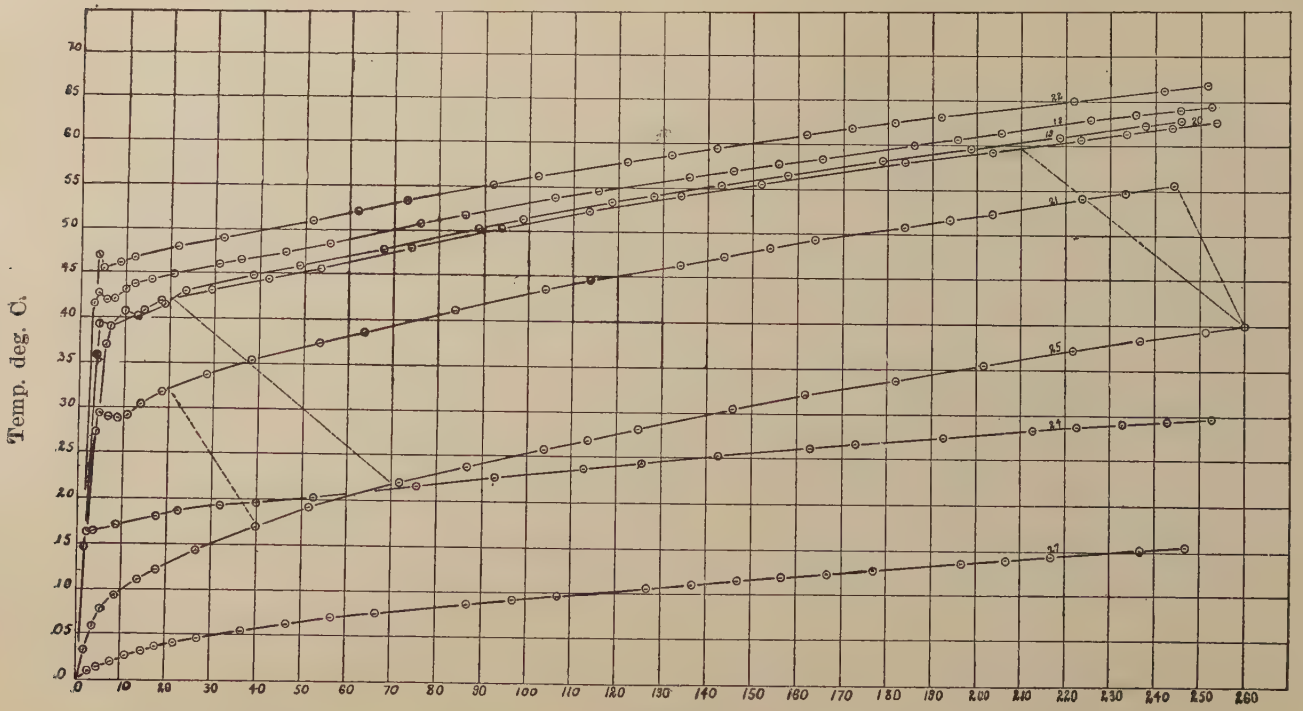

Figure 5

* Det. No. 30, see figure 6

Numbers on curves are the same as determination numbers, 20, 21, 22, 23 and 25 are for 0.250 M solutions. 24 and 27 are for 0.125 M solutions.

This factor will be the reciprocal ratio of their concentrations, since the speed of reaction, and hence the evolution of heat is proportional to the concentration. In this instance the factor is ½ for the 0.500 molar and 2 for the 0.125 molar in order to compare them with the determinations of 0.250 molar solutions. A transposition of this sort has been made with determinations 30 (with 0.500 molar solution) and 24 (with 0.125 molar solution) and the agreement is very good. The original curves for these determinations, as well as others with 0.500 molar and 0.125 molar solutions are shown in Figure 6.

The initial temperature for these determinations was 20 degrees C ±.03 degree with the exception of experiments 33 and 34 which were conducted at 25 degrees C for the purpose of estimating the temperature coefficient of the reaction so that if necessary a correction could be applied for the effect of the temperature change that occurs during the progress of the reaction. After taking into consideration that the energy change for the system decreases about 2.8% for a temperature rise of 5 degrees, the slopes of the curves at the two different temperatures, are so nearly the same that it is impossible to estimate a dependable temperature coefficient. It is therefore evident that the results here presented will not be measurably effected by the emperature change during the progress of the reaction and that these results will be applicable over the temperature range of 20 to 25 degrees without an error greater than .3%.

To demonstrate in another way that these curves are essentially the same differing only in that they represent different stages of the reaction, they have been compared by means of an empirical equation. It has been assumed that the ideal diffusion curve is one which represents the process in which instantaneous superposition without initial mixing occurs in this series of determinations, curve 27 seems to be nearest to this ideal. An impiracle equation which satisfies this curve between 10 and 247 minutes after diffusion begins within less than 0.001 degree is,

$$T = 0.05\ C\ t.^{584} \qquad (1)^*$$

where T is the temperature rise in degrees centigrade, C is consentration, t is time in minutes and .05 and .584 are constants. For the curves of determinations in which initial mixing occurs, so that a transposition of the curve is necessary for agreement with the ideal the expression,

$$T = .05\ C\ (t\text{-}x).^{584} + y \qquad (2)$$

may be applied, where T, C and t have the same meanings as in equation (1) and y is the temperature rise due to initial mixing in degrees C and x is the time interval of transposition to the ideal in minutes. With ideal conditions, x and y become zero and equation (2) becomes (1).

In equation (2) the quantity y may be determined either by extrapolating the long curvesegment which lies beyond the period of initial disturbance back to the origin, or by substituting the experimental values of T, C, t and x, and solving for y. Of these two procedures the latter is more exact; the extrapolation, however, is desirable, since the complete curve thus determined represents the ideal. The values of y determined by the two procedures then indicate the precision of this extrapolation.

*The exponential form of this equation was naturally suggested by the nature of the process.

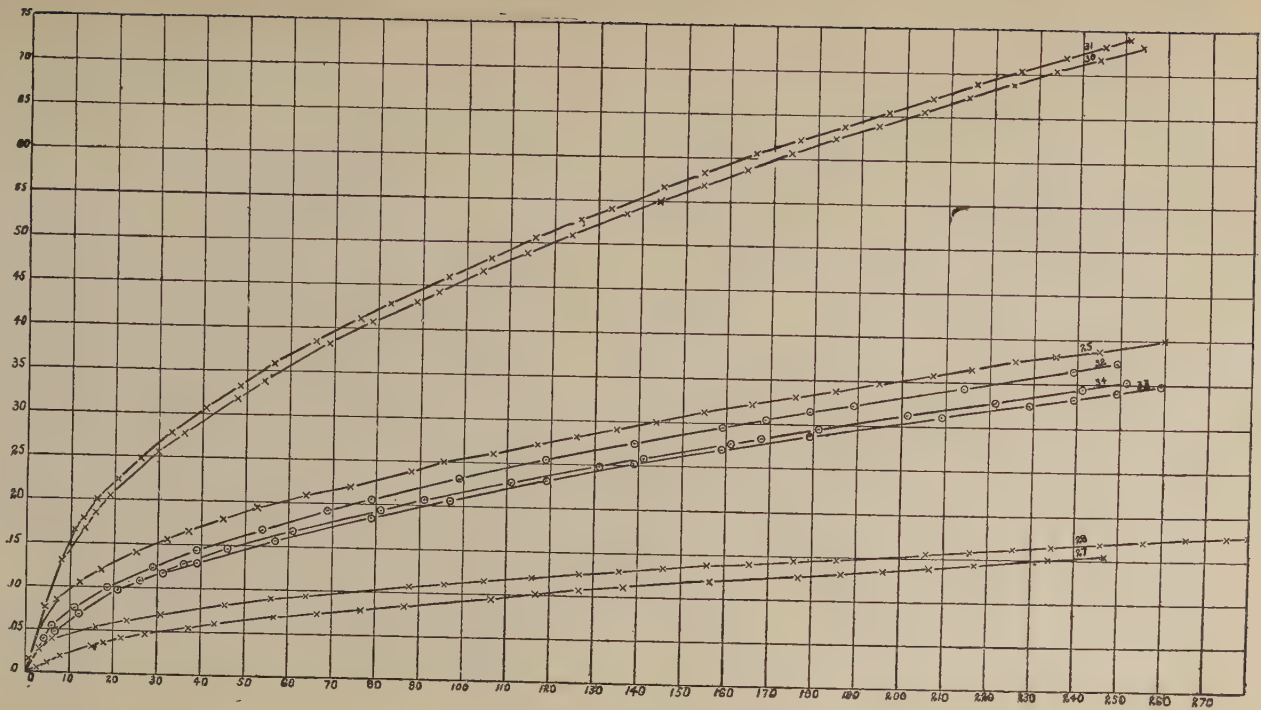

Figure 6

Numbers on curves are the same as determination numbers. 30 and 31 are for 0.500 M solutions and 27 and 29 are for 0.125 M solutions.

With respect to very nearly* all of the determinations of diffusion rates, the results have been compared by the procedure of superposing the derived curves. In a smaller number of cases, the formula for the ideal curve has been applied: where parallelism between the curves is closest it has not been thus applied, since in such cases its applicability was a foregone conclusion. These tests in the aggregate demonstrate conclusively that the heat of neutralization in the interdiffusion of hydrochloric acid and sodium hydroxide solutions under the varying conditions of these experiments — that is, within the temperature range of 20-25 degrees and for a range of concentration of from 0.125 to 0.500 molar — is evolved in a uniform manner which is defined by the equation of the ideal curve given above. The uniformity is so close that the probable variation is very near to the predetermined experimental error, represented by an extreme variation from parallelism between the curves of .002 degree or of 0.5 per cent of the mean temperature range measured. That this uniformity is not accidental — that is, is independent of the particular volume and configuration of the system used — is highly probable, taking into consideration the nature of the process, and assuming (on the evidence elsewhere presented** and upon that provided by the complete similarity in the behavior of solutions of widely different concentrations) that in all determinations the diffusion head, or the concentration of the ultimate reservoir of diffusing ions was constant in every case for the duration of the process. It is also highly probable that the regularity thus demonstrated for the behavior of hydrochloric acid and sodium hydroxide is characteristic of any other systems of interdiffusing electrolytes of comparable concentrations: from the nature of the process it is to be expected that all such diffusion systems will exhibit this exponential diminution of the rate at which heat is evolved, though the constants of the formulas applicable to different chemical systems would probably differ.

Pending the accumulation of more inclusive evidence, therefore, it may be held as highly probable that the typical behavior of interdiffusing solutions of moderately concentrated electrolytes, with respect to the evolution of reaction heat has been formulated with considerable precision; and as equally probable, therefore, that the rates of diffusion of the interacting ions is thus correctly represented. The explicit purpose of the research, consequently, has been fulfilled; and the first data provided for further detailed experimental investigation of similar and related phenomena.

It should, perhaps, be emphasized that this solitary result is not, probably, the most important consequence of the work. Not data alone, but a method of procedure applicable to the multiplication of such data, and by simple modification available for more particular examination of the superimposed effects here measured as a whole, is herewith presented; and it is not irrelevant to add that the mere demonstration of the possibility of determining with precision in a simple case the heat developed in a thermally inhomogeneous system promises much for the further useful extension of adiabatic technic in calorimetry and thus for the continued improvement of thermochemical methodology.

*The cases not yet examined in detail are so closely similar to corresponding cases minutely examined, that only the exact degree of their coincidence remains in doubt: its order of magnitude is apparent. **Page 10

THE HEAT CAPACITY OF THE SYSTEM

In order to determine the actual quantity of heat that has been evolved in any given instant, by the interdiffusion of the two solutions it is necessary to know the heat capacity of the calorimeter and the thermometer as well as that of the solutions. Since the calorimeter is gold plated copper and its cover is gold plated brass with vulcanite tubing extending from it and since the thermometer must be included an experimental determination of the heat capacity of the whole was considered more feasable than to attempt its calculation from data that might be at hand. The method and apparatus for this purpose was essentially the same as for the thermometer calibration.

A heating element with a measured amount of water was placed in the diffusion calorimeter and the number of joules of electricity necessary to raise the temperature of the system any desired number of degrees was determined. Joules divided by 4.183* gives the total number of calories put into the system. Then subtracting from the total the quantity taken up by the water and the heating coil and dividing by the temperature rise gives the heat capacity of the calorimeter and thermometer.

It was first necessary to construct a new heating element suitable for use in the diffusion calorimeter and to determine its heat capacity. The heating element was made of number 27 silk insulated and heavily shellacked manganin wire, wrapped on a shallow brass spool of 50 mm. inside diameter. The spool was then inclosed in a tight fitting brass tube and the seams sealed with solder. The leads were brought to the top of the water through a brass tube and through the air gap to the exterior through vulcanite tubing. The space around the manganin wire was filled, by suction, with paraffin.

The heat capacity of this element was determined in the calibration calorimeter by determining the quantity of heat necessary to change the temperature of the system through a temperature interval of about .5 degrees, first with the calibration system alone, and second with the heating element present. The difference in these two quantities divided by the temperature rise gives the heat capacity of the element.

These data are found in table 1, where determinations 2, 5 and 9 are with the calibration calorimeter, containing 1107.95 grams of water. Determinations 3 and 4 are the same with the addition of the heating element. Determinations 6 and 7 are with diffusion calorimeter, containing 819.91 grams of water and heated by the heating element of known water equivalent.

These determinations were carried on by one operator and the time readings, with few exceptions, were taken as the meniscus passed each .01 degree graduation mark: that is, these data were taken in the same way as the data for calibrating a thermometer and they have in fact been used as calibration data over the range here used. The correction for imperfect adiabaticity in each of the determinations was less than 0.0001 degrees and was neglected. Stirring was at the rate of 15 strokes per minute and caused no measurable error. Preperiods and post periods of an hour or more were taken for nearly all the experiments. In these periods there was no temperature

*International electrical joules per 20 degree gram calorie.

Det. Number	Potential across heating coil	Potential across 10 ohm standard	Resistance of heating coil	* Rrange in degrees C uncorrected	Time in seconds	Calories of heat evolved $H = \frac{E^2}{R} \frac{t}{4.183}$
Calibration Calorimeter with 1107.95 g. water						
2	2.29316	1.78164	12.871	20.50 - 21.00	6218	607.34 a 1
				20.47 - 20.78	3844	375.43 b 1
				20.45 - 20.78	4089	399.37 c 1
5	2.28340	1.77420	12.870	20.47 - 20.78	3885	376.25 b 2
				20.45 - 20.78	4144	401.42 c 2
9	2.26160	1.75740	12.870	20.50 - 21.00	6402	608.26 a 2
				20.47 - 20.78	3950	375.00 b 2
				20.45 - 20.78	4204	399.43 c 3
Calibration Calorimeter, Heating Element and 1107.95 g. water						
3	2.28600	1.77616	12.871	20.50 - 21.00	6348	616.20 d 1
				20.47 - 21.01	6855	665.40 e 1
4	2.28007	1.77616	12.871	20.50 - 21.00	6342	615.62 d 9
				20.47 - 21.01	6848	664.70 e 2
Diffusion Calorimeter with Heating Element.						
6	2.64552	1.61206	16.411	20.50 - 21.00	4465	455.2 f 1
7	2.64566	1.61208	16.411	20.50 - 21.00	4442	452.9 f 2

	Average	Maximum variation from mean
a's	607.80	.46 calories
b's	375.56	.69
c's	400.07	1.35
d's	615.91	.29
e's	665.05	.35
f's	454.05	1.15

* Readings were made to 0.0002 degrees.

change greater than 0.0004 degrees for a period of an hour and it usually remained under 0.0002 degrees. In table 1 the quantity of heat that has been developed for several different time intervals is given, this is merely to show the agreement of results, however only one time interval, corresponding to 20.50-21.00 degrees, is used in the calculations; It was determined by comparing it with a normal Baudin thermometer that had been standardized at the Bureau des Poids et Mesures. The precision of this comparison is about 0.0005 degrees, and the interval was found to be 0.4995 degrees. Determination number 5 is incomplete and therefore is not included in the calculations. Using the mean of determinations 2 and 9, and 3 and 4 we have for the heat capacity of the heating element,

$$\frac{615.91-607.78}{0.4995} = 16.28 \text{ gram calory units.}$$

Besides the heating element and water in the diffusion calorimeter was a light weight stirrer of copper, the heat capacity of which was calculated to be 0.86 calories ($\pm$ not more than 0.01 calories). Taking the heat capacity of water at this temperature as 0.9992 we have as a total for these three,

819.91 x 0.9992 = 819.25 heat capacity of water
16.28 heat capacity of heating element
.86 heat capacity of stirrer
836.39 total

and

(836.39 x 0.4995) + (Ht. Cap. Cal. x 0.4995) = 454.05 calories.
72.61 calories = heat capacity of diffusion calorimeter and thermometer.

The only other data necessary for the conversion of the diffusion rate into calories are found in tables 2 and 3.

Table 2.

Specific heat of NaOH and HCl, Heat of neutralization. *

Conc. M/L	NaOH [20]	HCl [21]	
.125	.992	.992	13558
.250	.978	.983	13618
.500	.968	.962	

Table 3.

Weights of solutions in each determination.

Det. No.	18	19	20	21	22	24	25	27	29
Weight NaOH	400.13	387.54	402.56	396.06	393.14	390.82	390.47	391.10	391.93
Weight HCl	400.03	387.40	399.97	395.84	393.15	391.44	390.60	391.57	390.82

*Interporlated from data at 18 and 32 degrees, taken from Landolt and Borenstein.

(20) Richards and Rowe: J. Am. Chem. Soc. 43, 770 (1921).

(21) Richards and Rowe: J. Am. Chem. Soc. 42, 1621 (1920).

Table 3 continued

Det. No.	30	31	33	34
Weight NaOH	392.13	391.48	391.38	391.58
Weight HCl	391.70	391.57	391.62	391.62

Summary

This investigation includes:

1. A brief discussion of the interdiffusion of electrolytes.
2. A description of a method and the apparatus for measuring the interdiffusion of solutions that evolve heat in the process of diffusion.
3. An illustration of the method with equal molar solution of hydrochloric acid and sodium hydroxide.
4. An equation is given that defines the curve of interdiffusion of hydrochloric acid and sodium hydroxide for concentrations between 0.125 and 0.500 molar at 20 to 25 degrees centigrade.
5. A precise measurement of temperatures in a thermally inhomogeneous system.
6. A preliminary announcement and brief description of an electrical method for the standardization of thermometers.
7. The heat capacity of the calorimeter system and other data for converting temperatures to gram calory units.

VITA

Allan Kay Smith was born near Anamosa, Iowa, January 18, 1895. He received his B. S. degree from Coe College in June 1919 and was a graduate student at Columbia University in the city of New York, under the faculty of pure science from September 1923 to June 1926, receiving his M. A. in June 1924. He was instructor in chemistry at Sioux Falls College 1919-1921, assistant professor in chemistry at Kansas State Teachers College of Pittsburg, Kansas, 1921-23 and assistant in chemistry at Columbia University 1924-26. He is a member of Phi Lambda Upsilon and Sigma Xi honorary societies.